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Acknowledgements

I would like to acknowledge, with thanks, the generous help and advice of Paul Storch, Senior Objects Conservator at the Daniels Objects Conservation Laboratory of the Minnesota Historical Society, who originally conceived of this guide and whose assistance made this guide possible; Professor Guy Gibbon, Department of Anthropology, University of Minnesota, for his advice and criticism; Ellery Frahm, University of Minnesota, for his information on electron microprobe analysis; and finally Tom Braun, Associate Conservator of Objects, Minnesota Historical Society; Andrea Berlin, University of Minnesota; and Ashutosh Singh, University of Minnesota, for their helpful comments on the first draft of this paper. In addition, I would like to thank the Minnesota Historical Society for allowing me lab space and generous resources to verify the chemical tests presented in this manual.

Introduction

Any archaeologist would agree that knowing the correct material makeup of an object is important when interpreting its use, origin, manufacture, date, and other cultural information. Therefore, incorrectly identifying the composition of an artifact may result in drastic misinterpretation of its use or purpose. Suppose an archaeologist excavating a site, which is in a region lacking native silver, finds artifacts of a silver-copper *alloy* and misidentifies them as copper. Let's also suppose that objects of silver have never been found at contemporaneous occupation sites in this region. By misidentifying these artifacts, the interpreter may overlook useful evidence for trade relations, site date, and inhabitants.

Many students of archaeology and archaeologists themselves oftentimes misidentify archaeological materials. This is due to the fact that material identification of archaeological artifacts is a difficult and time-consuming task. Resources and time are generally limited in the field, and visual characterization is the only material examination that an object may receive. However, the timely identification of important materials during excavation will have an impact on the direction of digging, the focusing of resources, and interpretation of the site.

Purpose

This guide is meant as a reference tool for practical archaeological materials characterization in the field and in the lab, and discusses simple visual, physical, and chemical tests that can be employed to correctly identify common archaeological materials. The basic attributes, chemical makeup, and terrestrial deterioration mechanisms of each material are also covered in this guide to give the reader a better understanding of material nature and how different environments affect it. This guide should not be limited to archaeological analyses. Museum curators, appraisers, art historians, and others will find the information presented in this manual to be informative and applicable.

Since every possible material cannot be covered in such a format, only the most common materials found at archaeological sites are accounted for. Plastics that are commonly found in modern historical sites of the Americas and Europe are covered in this guide, because identification literature for archaeologists on this topic is scarce. It is inevitable that some materials, such as aluminum, cannot be identified using this guide, and, in these cases, contacting a specialist or conservator is advised.

Layout

For convenience, this guide was written in outline form for quick reference. Materials are broken down by category, and each category is generally divided into three or four major sections: material description, deterioration, visual characterization, and chemical identification (where relevant). The decision tree, found on pages 34 & 35, should be employed as a characterization tool, because it outlines the identification process recommended by the author, and references sections relevant to each step in the process. This guide also includes a glossary of technical terms, which have been italicized throughout the text.

Notes on Visual Characterization

Such things as manufacture marks in glass, pores in lamellar bone, and corrosion products are difficult to observe with the unaided eye. Therefore, when visually examining material, it is always helpful to use a field lens or low powered microscope. A stereoscope is highly recommended because it allows one to examine contours and spatial relationships, features concerning manufacture technique and use wear.

A reference set made up of deteriorated and non-deteriorated representative samples of each material discussed in this guide should be employed for more accurate characterization. These samples need not be from an archaeological context, but archaeological materials are preferred. The ability to recognize a certain material correlates with the number of times one has seen it. However, this is usually not the case with alloy metal characterization, because of the numerous alloy corrosion products that may form on the surface.

Notes on Physical Characterization

By testing for presence or absence of certain physical characteristics, one can quickly and easily distinguish between specific materials. For example, an iron nail can be distinguished from a brass nail, by testing for magnetism. Pyrolysis, discussed in the plastic section, can be employed to distinguish between particular plastics, which burn and melt differently.

This guide does not cover density testing, which may be useful for characterizing materials with little or no deterioration present. Density testing requires an object to be free from foreign particulates and corrosion products, which are common on archaeological materials. Please consult with a conservator for more information concerning density testing.

Notes on Chemical Identification

Wet chemical testing is destructive, but often times necessary when dealing with materials such as metals, because they are difficult to visually distinguish. This guide offers directions for simple and inexpensive chemical identification tests for calcareous materials and common metals. These tests only identify presence of the matter being tested for, and not quantity. Therefore, it is always a good idea to test metal objects for presence of more than one metal.

As with visual characterization, it is important to use a reference set when employing qualitative chemical analysis. The reference set does not need to be made up of archaeological artifacts, but can be made up of a collection of modern materials. Low power microscopic examination will aid in correctly identifying test results.

If there are means, non-destructive instrumental analysis, such as scanning electron microprobe and x-ray fluorescence, may be employed not only to identify materials, but also to gain a plethora of other useful information. These instruments are available at many universities and research-oriented corporations. Contact a local conservator for further information about these procedures and where these instruments are available.

1. Bone and Ivory

1.a. *Description*

Bone and Ivory are made of both inorganic (calcium phosphate and other trace minerals) and organic proteinaceous materials. There are two basic types of bone structure. The first type is cortical, also called lamellar, bone, which is the smooth and hard outer laminate or surface layer of a bone. Lamellar bone, usually obtained from long bones, is generally used for tool making and carvings. The other type of structure is cancellous bone, which is the inner core of bone surrounding the central marrow cavity. Due to its characteristic porous structure, cancellous bone is not used as a carving material.

Ivory is similar to bone in chemical make-up, but it is composed primarily of 1:3 collagen:hydroxyapatite (*dentine*) compared to 1:2 collagen: hydroxyapatite in bone.
The chemical structure of teeth and tusks of mammals is the same regardless of species of origin. Thus, ivory, as defined in this guide, is any worked mammalian tooth or tusk.

1.b. Deterioration

1. Bone is more susceptible to deterioration than ivory, because it is has a less crystalline structure, and undergoes more chemical and mechanical treatment when being defleshed during processing, which catalyzes decay.
2. Chemical reactions of ivory and bone are the same during deterioration, because of composition similarity.
3. Acidic conditions will result in the leaching of bone minerals, causing bone to lose strength and rigidity.
4. Basic conditions will cause bone to become more brittle and friable because collagen and other proteins will breakdown.
5. Temperature variance and moisture can cause cracking and warping of bone.

1.c. Visual Characteristics

Spongy calcareous structure- a structure composed of large and irregular pores, which is characteristic of cortical bone.

Black, bluish gray, or white color- resulting from burning bone or ivory at high temperatures. Bleached white calcined bone results from extremely high temperatures being reached, such as the heat needed for cremation.

Minute pits or irregularities on surface- canals for blood vessel and nerve passage in lamellar bone. 10x or greater magnification from a hand lens or microscope will be an aid in observation of these features.

Black or brown color- Caused by staining from anaerobic peat bog conditions, although a variety of colors can arise from staining by different surrounding deposits.

1.d. Ivory/ Bone Distinction

In many cases archaeological ivory and bone in good condition can be distinguished by microscopic (10x magnification or greater) surface examination. Even though they have similar chemical compositions, bone and ivory have different cellular networks. Bone shows a coarse grain with characteristic lacunae as discussed above, while ivory exhibits a series of striations, or micro-canals, radiating from the center of the tusk. These striations appear in the form of cross-hatching or 'engine turnings.' Cross section examination may be needed for distinguishing between the two.

1.e. Chemical Characterization

There are no simple tests available that one can employ to easily identify bone. However, calcium carbonate in bone can be identified using the test outlined in section 4.d.

2. Leather

2.a. Description

Leather is a soft, flexible, and durable material produced from animal skin or hide that has been tanned or chemically treated in some other way for use. To understand the characteristics of leather, knowledge of animal skin in general is imperative.

Animal skin consists of a *collagen* membrane, which is itself composed of bundled fibers of collagen that, when in the presence of water, slide freely over each other. Skin has a flesh side and a hair side. The flesh side of the membrane is lined with fat, muscles, and blood vessels, while the hair side is lined with sweat glands and hair follicles, which make up the characteristic grain of leather.

During the manufacture of leather, the flesh and hair sides are removed from the skin, so as to delay the putrefaction of the material. A number of different reversible and irreversible treatments can be employed after this step, but all involve replacing the water in skin with something less volatile. *Tawing*, smoking, oiling, and salting are leather preparations that do not create a permanent chemical change to the skin, and ingredients from these treatments can be washed out during use (Sease, 1994). Tanning is an irreversible process that forms chemical bonds between the tanning medium and the collagen in skin. This treatment makes the skin resistant to water and also preserves its natural flexibility.

2.b. Deterioration

1. The susceptibility of leather to biological, physical, and chemical breakdown is so great, that it generally does not survive usual burial conditions.
2. Cold, dry, or wet stable environments may preserve leather.
3. A stable dry environment causes leather to lose its water content and lubricants causing cracking, shrinking, and brittleness.
4. Wet stable environments that are anaerobic and slightly acidic, such as bog conditions, deter biological breakdown.

5. Extremely salty and stable burial conditions retard biological breakdown, and leather found in these conditions is often well preserved.
6. An unstable wet environment will cause the hydrolysis of collagen, creating a weakening of the leather structure and eventual total decomposition. If this environment is aerobic, biological breakdown will also occur.
7. Leather does not survive land deposits with a pH above 6.4, due to the rapid hydrolysis of collagen above this pH (Cronyn, 1990).

2.c. Visual Characterization

Embrittled- due to loss of collagen lubricants in leather from a dry site. Water evaporates, and fats or oils may oxidize and cause the stiffening and shrinking of leather. Cracking and shrinking are typical of this type of deterioration.

Crumbling structure- caused by hydrolysis of collagen in a wet environment.

Black or dark- staining by tannates or other chemicals in the soil. This can also be brought about by the oxidation of the lubricating fats or oils in leather.

Grain pattern- seen on intact leather specimens, and made up of hair follicles.

3. Wood

3.a. Description

Wood is the hard fibrous skeletal tissue of higher green plants, and is composed mainly of xylem. It is anisotropic, meaning that it exhibits varying degrees of physical properties in different directions. There are two basic types of wood, softwood and hardwood, which can be distinguished from each other by density. The size of the vascular vessels (*phloem*) in a tree determines the density of the heartwood. In softwood trees, the vessels are fairly broad, resulting in low-density heartwood. In Hardwoods, the phloem is much narrower, which results in more dense heartwood.

3.b. Deterioration

1. As with all organic materials, wood decays by biological, physical, and chemical attack.
2. Due to this susceptibility, wood survives best in stable environments such as continuously wet or dry deposits with little change in temperature.
3. Wet environments usually deter aerobic biological deterioration of cellulose, in favor of slow anaerobic breakdown.
4. Acidic bog environments, with a pH less than 3.0 will inhibit anaerobic activity, causing exceptional preservation.
5. Wet alkaline deposits will bring about the fossilization of wood by calcium carbonate replacement, and, in some cases, fossilization can occur within a few hundred years (Cronyn, 1990).
6. Temperature and moisture variance will cause warping or cracking of wood.

3.c. Visual Characterization

Concentric radiating rings- rings radiate outward from a central stem. This characteristic is particular for wood.

Pronounced growth rings- characteristic of hardwood specimens, which also exhibit miniscule phloem. Comparing with reference samples will help in distinguishing between hard and softwood.

Tubular Vessels or small holes on surface- characteristic of softwoods, which tend to have less pronounced growth rings.

Black surface- decay caused by fungi hyphae or staining by iron tannates in the soil. Black colored wood is often mistaken for char, and is distinguished from char by lack of a chalky surface.

Grey or light colored surface- due to a type of wood decay in which the fungus digests the lignin in wood and leaves the white cellulose behind. An unstable, spongy or fragile structure results from this type of decay.

3.d. Species Identification

A specialist in the field should carry out species identification. While some specimens can be identified without destructive testing, a cross-section sample is usually necessary for precise identification of species.

4. SHELL

4.a. Description

Shell, as referred to in this paper, is the outer protective covering of marine, freshwater, or land mollusks. It consists primarily of calcium carbonate, covered by a thin proteinaceous exterior membrane. Calcium carbonate is excreted by the mantle of a mollusk, and is built up in the form of layers over the organism's lifetime. Shell has been commonly used, since the earliest of times, as ornamentation and for tools.

4.b. Deterioration

1. Archaeological shell is generally found to be in good condition unless in an acidic environment.
2. A low pH environment will lead to the dissolution of calcium carbonate, and a powdery and friable shell will result.
3. Water moving through large concentrations of shell may dissolve and redeposit calcium carbonate on adjacent artifacts or the shells themselves in the form of *caliche* encrustations, or cement them together. (Storch, 1997)

4.c. Visual Characterization

White or off-white- most shells, especially fresh water species, are these colors due to lack of pigmentation.

Color mottling- common trait of salt water shell, and caused by pigmentation deposited in the shell structure during the mollusk's lifetime. May also be due to staining from periods of extended burial.

Lamellar composition- made up of layers of calcium carbonate varying in thickness. The thickness of each layer depends on many factors, such as different times of the year or availability of calcium in the environment. Like tree rings, these layers are useful for seasonal studies of the environment in which the mollusk lived.

Chalky or powdery surface- indication of an advanced state of deterioration. This commonly occurs in an acidic wet environment, which will dissolve shell leaving a non-adherent surface. Shell in this state often has more pronounced lamellar striations.

Iridescent non-deteriorated surface- characteristic of the inner layer of shell, called the Mother-of-pearl, commonly used for decorative purposes, and harvested from many different fresh and salt water mollusks. Freshwater shells are usually not as iridescent or brilliant as saltwater shells.

4.d. Chemical Characterization

There is not a specific test that can be used to distinguish shell from other calcium carbonate materials, such as bone. However, a simple test involving aqueous acid can be utilized to test for calcium carbonate.

Calcium carbonate presence

This test is performed by placing a drop of acid directly onto the sample. Keep in mind that acid will etch the material and cause pitting. For this reason, an inconspicuous spot should be chosen for testing.

Theory

Calcium carbonate is dissolved by acid to produce visible effervescence of carbon dioxide. Dissolution of calcium carbonate with sulfuric acid is shown below.

$$CaCO_{3\,(s)} + H_2SO_{4\,(aq)} \longrightarrow Ca^{2+}_{(aq)} + SO_4{}^{2-}_{(aq)} + H_20_{(l)} + CO_{2\,(g)}\uparrow$$

Equipment

Glassware
Any strong acid, such as nitric, hydrochloric, or sulfuric acid
Deionized water
Gloves and goggles

Instructions

Refer to appendices I and II for chemical safety information and waste disposal associated with this procedure.

1. Place a drop of acid on the shell object to be tested, and watch for instant effervescence in the form of small bubbles. If no effervescence occurs, the test result is negative.
2. Immediately after observation, rinse the sample well with water to remove all traces of acid.

5. Glass

5.a. Description

Glass is an amorphous solid consisting of a fusion of *acidic* and *basic oxides*. The major constituent of glass is silicon dioxide, which forms the fundamental molecular structure. Basic oxides are added primarily to lower the melting point of silica, but the type of each oxide and the production process influences the different chemical and physical properties of the resultant glass. These properties include hardness, light refraction (refractive index), stability, color, etc. The most common basic oxides found in archaeological glass are soda (Na_2CO_3), potash (K_2CO_3), lime (CaO), and alumina (Al_2O_3).

5.b. Deterioration

1. Resistant to deterioration in dry ambient conditions.
2. Exposure to moisture may cause preferential leaching and diffusion of alkali ions (basic oxides) across the porous silica network at the surface of glass (Pannell*, 1996*).
3. Highly alkaline soils (pH>8.0), in the presence of groundwater, will increase the rate of attack on glass.
4. Higher temperatures will increase the rate of glass decomposition.
5. Glass with too little silica content is not stable to moisture, because of a weak silica network (Cronyn, 1990).

5.c. Visual Characterization

Transparence or translucence- apparent when the body of the object is viewed against a bright light source.

Structure irregularities- small gas bubbles, streaks of different opacity or color, or small opaque inclusions, all of which were created during manufacture.

Iridescence- distinguishing characteristic of glass artifacts. It is caused by the formation of many thin layers of mainly amorphous silica, due to the loss of alkali constituents. Each of these layers refracts light in different directions that are perceived by the eye as iridescence. However, if there is a high percentage of water in the glass upon excavation, the iridescence disappears due to the masking of refraction differences between layers.

Opacity- can occur when clear glass undergoes chemical or physical changes caused by deterioration, but is also created during manufacture. Opacity caused by deterioration is the advanced form of iridescence, where so many layers of glass have formed that the object absorbs light rather than refracting it. Rough, powdery or flaking surfaces may be seen on specimens turned opaque by deterioration. Manufactured opaque glasses contain additives, like certain metal oxides, to make them such.

Pitting- minute cavities due to select areas of glass being leached of alkali ions. Larger pits commonly have a dull or iridescent interior surface. Many minute pits on an object cause roughness of the surface.

Crizzling-a network of fine hair-line cracks occurring on the surface of the glass. Crizzling is a distinct feature of glass deterioration, and is caused by the leaching of alkali ions on the glass surface and physical strain brought about by variance in moisture or external forces. Glass manufactured with excess basic oxides commonly exhibits crizzling after extended periods of burial.

Weeping- a phenomenon occurring on post excavation glass which has been poorly manufactured. Reappearing water droplets seen on the surface after drying is indicative of weeping, and are formed by an exterior hygroscopic film of sodium and potassium carbonates. Water will continue to leach out more sodium and potassium ions in the process of weeping, leading to structural weakness in the glass.

Chalky crust or mass- indicates severe state of deterioration, in which almost all the basic oxides are leached out, leaving only silica. A crystalline structure composed entirely of fused silica is extremely weak, and an object in this state will often be hard to identify as glass.

6. Ceramics

6.a. Description

Ceramic is a broad term used to define objects of fired *clay*. Due to its plasticity when hydrated, clay is an excellent medium for sculpting, and when dehydrated, it becomes quite strong. Examples of this are mudbrick or adobe. The physical properties of a particular ceramic object depend on firing conditions, clay make-up, and surface treatments.

Filler

Often times unprocessed clay is too plastic for working, and a filler, called temper, is added to make it better hold its shape. Fillers are also added to form a porous structure, which, during firing, does not melt and facilitates dehydration. If moisture is unable to evacuate quickly enough during firing, cracking or an explosion of the ceramic will occur. Common temper materials for archaeological ceramics are quartz sand, calcined flint, shell, and *grog.*

Firing conditions

The temperature, duration of time, and firing atmosphere all have radical effects on the final properties of the ceramic. Temperature and time are the most important of the three in terms of physical strength and durability. There is a certain temperature, which varies with different types of clay, called the maturing temperature, at which clay particles will condense to produce the densest structure without completely melting and changing shape. If this point is not reached and sustained during the firing process, crumbly or weak ceramics will result. If the clay is matured, a harder and more durable product will form.

Surface treatments

Burnishing, polishing, incising, impressing, glossing, glazing, and slipping are just a few of the surface treatments that are utilized for the purpose of modifying physical or aesthetic qualities of ceramics. Slipping and glazing are both common treatments. Slip is a thin ornamental coating of fine particles applied to the dry clay before firing, and is, in most cases, a different color than the underlying clay object. Glaze is a glasslike surface fused to the exterior of a ceramic object at high temperatures, and is applied both for aesthetic and practical purposes, such as water resistance.

Types of Ceramic materials:

1. **Terracotta** (material)- any ceramic made of non-matured clay, which is tempered with fillers that are intended to modify plasticity rather than affect melting point. This refers to clay fired below 1000°C (Cronyn, 1990).
2. **Earthenware** (object genre)- matured terracotta that is fired between 1000°C and 1200°C. Bricks and tiles fit into the category.
3. **Stoneware** (object genre)- made from a mixture of quartz and feldspar containing clays. This type of ceramic is usually glazed and fired between 1200 °C to 1300 °C. Unglazed stoneware is normally white, gray or light brown (Hodges, 1976).
4. **Vitreous China** (object genre)- a type of stoneware that fires opaque white and is particularly dense.
5. **Bone China** (material)- a type of white and translucent stoneware named after the ox-bone temper that is used as a flux in the ceramic.

6.b. Deterioration

1. Due to the many variances in composition, certain ceramics will react differently to environmental conditions.
2. Matured ceramics will generally survive normal environmental conditions, because they are resistant to chemical and biological breakdown.
3. Physical stress during burial leads to the cracking or breaking of ceramic objects, and they are commonly found in broken condition.
4. Low-fired ceramics, such as terracotta, are prone to attack by soluble salts and moisture in a wet environment. Soluble salts that enter a ceramic body can

recrystallize upon drying and cause internal stress, leading to softening of the body and surface deterioration in the form of flaking or dissolution.

5. Soluble salts in wet conditions will also attack porous or incomplete glazes by the same mechanism as described above, and lead to flaking or cracking of the glaze.
6. Acidic conditions will dissolve calcareous tempers, such as shell or bone, leading to a weakened ceramic structure.

6.c. Visual Characterization

Caliche encrustations- alkaline burial environments may cause the deposition calcium carbonate crusts on ceramics.

Surface pitting or flaking- either dissolution of a low fired ceramic or soluble salt recrystallization will cause the surface to take on this appearance. This type of deterioration commonly occurs in wet unstable environments.

Angular sherds- matured ceramics tend to break in a geometric pattern.

Granular inclusions- denotes filler, which may be inorganic or organic. Filler is usually a different color than the clay body.

White glossy body- characteristic of vitreous or bone china. Bone china is translucent, while vitreous china is opaque.

Glaze- can be applied to any ceramic fired above 1000^{o}C. Physical stress or chemical deterioration can cause glazes to crack in web-like patterns.

Concentric striations on inner or outer surface- indicative of wheel made ceramics.

7. Copper and its Alloys

7.a. Description

Copper is a relatively soft, reddish yellow, and ductile metal. It is found in small deposits as *native* metal, but more commonly in ores containing sulfides, arsenides, chlorides, and carbonates. Due to its relative softness, copper is commonly alloyed with zinc or tin to make a harder product. The exteriors of copper alloys are often gilded, plated, or chemically patinated.

Copper-tin alloys

An alloy of copper and 1-10% tin is called bronze, and is reddish-brown in color. Up to 10% lead is sometimes added to soften the alloy, which is useful for fine casting (Sease, 1992). However, lead is not miscible in molten bronze, and, as a result, small globules of lead are trapped in the alloy structure upon cooling. An alloy of copper with approximately 30% tin is called speculum, which is hard, brittle, and white in appearance. Speculum was commonly used for mirrors in antiquity, because of its ability to take a high polish.

Copper-zinc alloys

The addition of up to 40% zinc to copper creates an alloy known as brass. Brass is a yellow metal, which becomes more yellow with increasing amounts of zinc up to 20 percent, but then turns whiter with a greater percentage (Cronyn, 1990).

7.b. Deterioration

Many chemical reactions take place on archaeological copper or alloy objects, therefore, only the most common forms of *corrosion* are discussed here.

1. Copper and copper alloys are frequently found well preserved in the absence of an aerobic saline environment, because of the lack of chloride ions.
2. Copper and its alloys deposited in a saline environment will form copper chloride minerals, which are unstable and perpetuated in the presence of oxygen and moisture.
3. Post excavation artifacts having active chloride induced corrosion are said to have "bronze disease." Bronze disease, if left unchecked, can result in pitting, and the complete disintegration of an object.
4. Sulfur ions in the environment react with copper and generally produce an even protective *patina*, but may also produce non-protective and uneven crusts.
5. Copper carbonates can be formed by reactions of copper with carbonic acids present in the soil. This type of corrosion will lead to either an even patina or an uneven crust.

7.c. Visual Characterization

Visual identification of copper and its alloys is difficult because of the many different corrosion products and the appearance they take on. Keep in mind that plating or *gilding* of silver, gold, or tin is common with decorative copper objects, and may be obscured by corrosion products of the underlying copper. On the other hand, plating or gilding might obscure the underlying metal causing misinterpretation.

Non-corroded appearance- copper in this form is usually found in an anaerobic wet environment, which limits the *oxidation* of copper.

Green or greenish/blue crust- an uneven encrustation usually consisting of malachite (copper carbonate) and copper chlorides, and usually found in a wet aerobic saline environment. A crumbly, powdery, or warty surface is typical.

Red, black, or brown patina- the result of slow corrosion consisting of copper oxides and copper sulfates/sulfides. Characterized by either a lustrous or dull surface. This color patina may be produced by extended atmospheric exposure, or burial in a stratum composed mostly of organic matter.

Green or blue patina- the result of slow corrosion usually consisting of copper (I) or (II) carbonates or copper (II) sulfate.

Pitting or patchy surface disrupting a smooth patina- alloyed copper corrosion may be patchy/warty or pitted if the alloy is not evenly distributed in the object. *Anodic sacrifice* of a less *noble* metal in the alloy causes this to occur. These oxidized metals take on a powdery gray or white appearance, which may or may not be easily seen on the surface.

Fine cracking- Speculum has a distinctive corrosion pattern, since it is brittle, that involves fine cracking, sometimes in the form of concentric circles. Cracking is caused by stress put on the metal when mineralization, leading to expansion, takes place.

White metal surface- the original surface of a bronze object may appear tinned. In some cases, tin is preserved at expense of copper even though copper is more noble (Cronyn, 1990).

7.d. Chemical Identification

7.d.1. Indicator Paper

A Cuprotesmo [Macherey-Nagel] indicator paper is moistened with de-ionized water and applied to the surface of the artifact or corrosion products can be scraped off onto the indicator. If copper^{2+} is present, the paper will turn a purple-pink color. Although not used by the author of this paper, this test seems to be the simplest for identification of copper in the field, posing no safety issues. See appendix IV for U.S. suppliers of this product.

7.d.2. Copper-Amine Indication (an adaptation of Odegaard et al, 2000)

This test is performed by either scratching off a sizeable amount of corrosion product from the sample onto a piece of filter paper, or by placing a drop of acid directly onto the sample and wicking the acidic solution up with filter paper. If the latter is chosen, keep in mind that nitric acid will etch the object, therefore an inconspicuous spot should be chosen for testing.

<u>Theory</u>

Nitric acid is used to oxidize copper and form a copper nitrate solution. The acidic copper solution is then exposed to concentrated ammonia fumes, which form a blue copper-amine complex.

$$Cu^{2+}_{(aq)} + 6NH_{3(g)} \longrightarrow [Cu(NH_3)_6]^{2+}_{(aq)}$$

Equipment
Glassware
Filter paper
Deionized water
Concentrated or 8M nitric acid (analytical grade preferred)
Ammonium hydroxide (household ammonia)
Gloves and goggles
Fume hood, or other means of adequate ventilation

Instructions

Perform this test under a fume hood. Refer to appendices I and II for chemical safety information and waste disposal associated with this procedure.

1. Prepare an 8M nitric acid solution by carefully adding a small amount of analytical grade concentrated nitric acid to an equal amount of distilled water. **Acid must always be added to water**. Option 2a or 2b may be chosen for the next step.
2a. Scrape off a sizeable amount of corrosion product from the sample onto a piece of filter paper, and place a drop of the 8M nitric acid solution made in step 1 on the paper.
2b. Place a tiny drop 8M nitric acid on an inconspicuous area of the sample. Effervescence should occur, and after about 30 seconds wick the liquid onto a piece of filter paper.
3. If step 2b was chosen, thoroughly wash off the sample with deionized water to remove all traces of acid. With tweezers, hold the filter paper over the mouth of an open container of ammonium hydroxide allowing ammonia fumes to come in contact with the paper. During this time white vapors will evolve. Look for a blue or blue-green stain on the paper, which indicates that the sample contains copper.

8. SILVER

8.a. Description

Silver is a white, soft, and lustrous metal found in *native* form in small quantities. The majority of silver exists naturally in mineral form, which is usually Argenite (Ag_2S) and cerargyrite ($AgCl$). Silver has been a favorite among jewelers since ancient times because it is malleable, resistant to corrosion, and capable of taking a high polish. However, pure silver is too soft for practical use and is often alloyed with other metals, copper being favored, to make it stronger. Silver is also common plating metal.

8.b. Deterioration

1. Silver, being a noble metal, doesn't react with oxygen.
2. Silver reacts with sulfur in the atmosphere to produce silver sulfide, which is a protective patina that slowly accumulates over time.
3. Buried silver reacts with the sulfur, bromine, and chloride ions present, which produce the different effects explained below.

4. In the absence of chlorides or bromides, silver generally produces a silver sulfide patina.
5. Buried silver in the presence of chlorides from a saline environment forms a semi-protective layer of cerargyrite, or horn silver.
6. An environment with a high corrosion potential, due to excess chlorides, may permeate the protective layer of silver and cause disfiguration in the form of a hard swollen crust.
7. In the presence of bromides, which are created from the break down of organic matter, bromyrite (AgBr) can form, and may cause disfigurement of the object in severe cases.

8.c. Visual Characterization

Corrosion products of pure silver will have a white, purplish black, or gray appearance. Keep in mind that silver plating will give an object the appearance of being silver. Corrosion of the underlying metal causing loss of the silver surface will give clues to help identify the object as being plated.

Black or dark purple patina- extended atmospheric exposure or non-saline wet or dry environments will produce this. The patina is composed of a silver sulfide protective layer, which may be dull or shiny in appearance.

Black, gray, or brown crust- an advanced state of corrosion typified by a hard crust with disfiguring and swelling of the object surface. This crust is a result of chlorides, bromides and sulfides, all of which are common in a saline environment, attacking the metal. Chlorides in the soil will react with silver to produce a non-protective layer of horn silver (AgCl). A brown crust will develop in the presence of excess bromine that can be created by deteriorating organic matter.

Appearance of copper corrosion- copper corrosion may cover the entire surface of a silver-copper alloy, giving it the appearance of corroded copper. In a less advanced form, spots of copper corrosion may appear on the surface. Being that copper has a higher reduction potential than silver, copper is preferentially corroded through anodic sacrifice in the presence of an *electrolyte* (moisture).

8.d. Chemical Identification

Silver Chromate indication (an adaptation of Plenderlieth and Werner, 1971)
This test is performed by placing a drop of acid directly onto the sample, keep in mind that sulfuric acid will etch the object, therefore an inconspicuous spot should be chosen for testing.

Theory

Chromium trioxide, in the presence of sulfuric acid, combines with silver to produce red silver chromate.

$$2\ Ag_{(s)} + Cr_2O_{3(s)} \xrightarrow{H2SO4} Ag_2Cr_2O_{4(s)}$$

Equipment
Glassware
Chromium trioxide crystals
15% sulfuric acid
Deionized water
Ammonium hydroxide (household ammonia)
Gloves and goggles

Instructions

Refer to Appendices I and II for chemical safety information and waste disposal associated with this procedure.

1. Place a drop of 15% sulfuric acid on a smooth or clean surface of the object to be tested.
2. Add a tiny crystal of chromium trioxide to the drop, and let stand for 1 minute.
3. Wash off crystal and surrounding solution with deionized water.
4. A red stain will be apparent if silver is present in the object. Microscopic examination may be needed to confirm presence or absence of the red stain.
5. To remove the stain, wash with ammonia and follow with thorough washing in deionized water.

9. GOLD

9.a. Description

Gold is rich yellow, malleable, and dense metal that is found more commonly in native form than as an ore. However, native gold is rarely found in pure form, and is ordinarily combined with silver or copper and trace amounts of other metals. Being that gold is exceptionally malleable, it is favored for fine and detailed metalwork, such as jewelry.

Gold is commonly alloyed with other metals to make it harder or because its availability is limited. An alloy with silver produces a white or pale product. The amount of silver present is proportional to the paleness of the gold alloy. Hence, electrum, which is a gold alloy that contains approximately 30% silver, is nearly white in appearance. Copper is also combined with gold to produce a reddish or warm yellow alloy. Many objects composed of this alloy are *pickled* to create a surface of pure gold.

9.b. Deterioration

1. The nobility of gold prevents it from naturally corroding.
2. While pure gold doesn't corrode, other metals present in a gold alloy may. This could cause cracking of the object if the percentage of alloy metal is high enough.
3. Gold leaf or plating in an archaeological context is extremely susceptible to lifting of flaking, because of the physical stress associated with the expansion of the base

metal. Also, the *sizing* of gold leaf is prone to deteriorate, causing loss of adhesion of gold to the object surface.

9.c. Visual Characterization

Non-corroded - pure gold is rather easy to visually identify because it is resistant to corrosion, and has a high density.

Copper corrosion- A gold-copper alloy may look like copper, if copper corrosion products appear at the surface of the object.

Silver corrosion- same effect as above, except occurring with gold-silver alloys.

Flaking or cracking surface- what seems to be a gold object may actually gilded. Flaking or cracking is due to sizing deterioration or internal stress caused by corrosion of the underlying metal.

Scratches on surface- pure gold is an extremely soft metal, which is easily scratched by many materials. Minute scratches are often times apparent on archaeological objects, and can be viewed with low magnification, such as a hand lens.

9.d. Chemical Identification

Safe and simple chemical tests for gold are not available for gold characterization. In most cases, visual identification is sufficient.

10. Iron

10.a. Description

Iron is a silver-white, lustrous, and not particularly hard metal. Native iron is rare because it readily oxidizes. In mineral form, however, it compromises 4.7% of the earth's crust (Zooidal, 1997). Most archaeological artifacts are technically steel, iron alloyed with a low percentage of carbon. The common types of archaeological iron are cast iron, containing 2.5%-5% carbon, and wrought iron, which contains less than .85% carbon (Cronyn, 1990). The more carbon content an alloy has, the harder and grayer it becomes. Hence, cast iron is a hard, gray, and non-workable alloy, and wrought iron is a softer and weaker alloy used for forging or welding. Recent archaeological artifacts, such as American colonial remains, are commonly plated with zinc or tin to prevent corrosion.

10.b. Deterioration

1. The corrosion of iron is a complex and not wholly understood phenomenon.
2. The most common form of corrosion is the oxidation of iron in the presence of moisture to form what is commonly known as rust. Rust is a number of different minerals consisting primarily of iron, oxygen, and hydrogen. This type of corrosion layer is non-protective due to its porous and non-uniform nature. Any type of

environment, unless otherwise noted below, with the presence of oxygen can create this type of corrosion.

3. In the case of buried iron, corrosion products may combine with particulate matter surrounding them, such as sand grains, wood, textiles, etc.
4. Iron chlorides are a common corrosion product generally in the form of a crust that self-perpetuates in the presence of moisture and oxygen. It occurs when iron is exposed to chloride ions from an aerobic saline environment. Swelling, cracking, or spelling of the crust is common.
5. Hematite ($\alpha-Fe_2O_3$) is a protective, thin, and non-disfiguring corrosion layer that forms on iron heated to a temperature of 200° C or higher. It is often times found on archaeological iron that has been in a fire.
6. Wet anaerobic organic environments provide an excess of phosphates that react with iron to produce thin coatings of vigilante ($Fe_2(PO_4)_2.8H_2O$), a protective layer.
7. Organic deposits that are aerobic can form thin protective coatings of phenol iron complexes (e.g. iron-tannates)
8. Anaerobic wet environments rich in sulfur reducing bacteria cause iron (II) sulfide to form, which is another form of a thin protective corrosion layer.

10.c. Visual Characterization

Iron corrosion products occur in a rainbow of colors, including green, yellow, blue, red, bright orange, black, and brown. The most common colors of buried archaeological iron are black, reddish-yellow, and orange. These colors are generally indicative of magnetite (Fe_3O_4), goethite ($\alpha-$Food), and hematite ($\alpha-Fe_2O_3$) respectively, which are ferric (Fe^{+3}) oxides. Common characteristics of an advanced state of corrosion are: a warty surface appearance with embedded particulates such as those described above, spelling, and cracking of crust.

Bulky red/brown/white mass or crust- typical of iron excavated from a moist aerobic environment. This type of non-protective corrosion is composed mainly of calcium carbonates, iron oxides, iron chlorides, and particulate matter. It is characterized by a powdery or crumbly surface. A white or off-white crust is due to the formation of calcium carbonates present in alkaline soil. Since this is an advanced state of corrosion, the metal core may not be preserved.

Black or blue hard and dull or shiny surface- characteristic of iron (II) sulfide, phenol iron complexes, or iron phosphate. This type of corrosion is common with iron deposited in the presence of organic matter. An object in this state may seem to be non-corroded.

Matte or red shiny surface- characteristic of hematite formed by heating iron to temperatures in excess of 200°C. This type of corrosion is characteristic of iron that has been in a fire.

Bright orange surface or bulky crust- attributed to aragonite ($\beta-$Food), which is a form of active ferrous oxide corrosion that is initiated by moisture and/or oxygen, and often associated with chloride corrosion.

Silver surface with appearance of white metal corrosion- typical of an non-corroded or slightly corroded object that has been *plated* with *white metal*. However, this plating is commonly masked by iron corrosion products, or has completely mineralized due to anodic sacrifice. Architectural items or cookware are commonly plated with white metal.

10.d. Magnetism

The best and easiest way to identify iron is to check for magnetism. Since many corrosion products aren't magnetic, magnetic examination will also indicate how much core metal is left of an object.

10.e. Chemical Identification

Iron (III) chloride indication (an adaptation of Odegaard et al, 2000)

Theory
Iron (III) reacts with chloride ions to produce iron (III) chloride, which is yellow.

$$2Fe^{3+}_{(aq)} + 6HCl_{(aq)} \longrightarrow 2\,FeCl_{3\,(aq)} + 3\,H_{2\,(g)}$$

Equipment
Glassware
Spotting plate
Concentrated hydrochloric (muriatic) acid
Gloves and goggles

Instructions
Refer to Appendices I and II for chemical safety information and waste disposal associated with this procedure.

1. Scrape a few fragments of corrosion product from the sample onto a glass plate.
2. Place a drop of hydrochloric acid over the sample fragments.
3. Allow time (up to five minutes) for reaction to take place.
4. The corrosion products will dissolve and form a yellow solution when iron is present in the sample.

11. Lead

11.a. Description

Lead is a soft, bright, and bluish-gray metal. Its low melting point and softness makes it an easily cast metal. Cast lead may contain impurities such as silver, which come from the same ore type, or chlorides and sulfur, which are characteristic of low-grade lead (Cronyn, 1990). Prior to modern times, lead was alloyed with tin and small amounts of other metals to produce pewter, which is discussed further in section 12.a.

11.b. Deterioration

1. Lead *tarnishes* quickly in ambient museum conditions from a bluish gray color to a grayish white (Plenderlieth and Werner, 1971). A grayish white color is indicative of lead oxide (PbO), which acts as a protective layer for the underlying metal.
2. Lead sulfides (PbS) may form if sulfur is present in the atmosphere.
3. Buried archaeological lead may contain lead sulfide, lead oxide, basic lead carbonate ($PbCO_3$), or lead carbonate ($2PbCO_3.Pb(OH)_2$), in the form of either a non-protective and loosely adherent powdery layer or a compact protective layer.
4. Basic lead carbonate formation is due to organic acids reacting with lead in alkaline soil.
5. Cracking and surface deformation mark advanced stages of corrosion.

11.c. Visual Characterization

Tin and lead corrosion products are visually hard to distinguish from each other, and, for that reason, testing beyond visual examination is needed to distinguish between the two.

Dull grayish white or brown surface- A grayish white surface is characteristic of lead oxide, while a brown color is the result of small amounts of lead sulfide in the lead oxide corrosion layer. Well preserved specimens commonly exhibit this type of condition.

Black rough or smooth surface- characteristic of a lead sulfide layer commonly associated with burial in anaerobic deposits that contain *sulfur reducing bacteria* or extended exposure to a polluted atmosphere.

Grayish white or white crust- common in wet alkaline environments where carbonic acid is present to form lead carbonates (Cronyn, 204). This crust most likely contains lead sulfides, lead oxides, and lead carbonates. A warty, non-adherent, or swelled surface is indicative of this type of corrosion.

Surface roughness (especially on the edges)- typical of advanced states of corrosion due to any of the factors above, and usually found in wet aerobic environments, which catalyze corrosion. Edges of the object may look worn away.

Cracking- Small fractures may be seen on the sample, due to stress caused by mineralization. An object in this condition is in an advanced stage of decay, and may crumble if it is not handled with care.

11.d. Tin/Lead Distinction

Due to its particular softness, lead leaves a black streak when rubbed on white paper, while tin doesn't. Make sure the core of the metal is tested, and not the powdery corrosion products.

11.e. Chemical Identification

11.e.1. Spot-test Paper Indicator

An indicator paper by the name of Plumbtesmo [Macherey-Nagel] is moistened with de-ionized water and applied to the surface of the artifact, and, if lead is present, the paper will turn a purple-pink color. This test seems to be the simplest and safest for chemical analysis of lead in the field, but may not fit in the budget of a normal excavation. See appendix IV for U.S. suppliers of this product.

11.e.2. Lead-iodide Indication (an adaptation of Odegaard et al, 2000)

This test is performed by placing an acidified piece of filter paper directly onto the sample. Keep in mind that nitric acid will etch the object, therefore an inconspicuous spot should be chosen for testing.

<u>Theory</u>

Lead is oxidized by nitric acid forming an acidic lead nitrate solution. Potassium iodide is then added to the solution, which will react with lead to form lead iodide (bright yellow).

$$Pb_{(s)} + HNO_{3\,(aq)} \longrightarrow Pb^{2+}{}_{(aq)} + KI_{(aq)} \longrightarrow PbI_{2\,(s)}$$

<u>Equipment</u>

Glassware
Stainless steel tweezers
Filter paper
Deionized water
Concentrated or .5M nitric acid (HNO3)
Potassium Iodide (KI)
Gloves and goggles

<u>Procedure</u>

Refer to Appendices I and II for chemical safety information and waste disposal associated with this procedure.

1. Prepare a 0.5M solution of nitric acid by slowly pouring 1mL concentrated nitric acid into 31 ml water. **Always add acid to water**.
2. Prepare a 10% potassium iodide solution by dissolving 1g of potassium iodide in 9 ml of water.
3. Dip a piece of filter paper in the .5M HNO3 solution prepared in step #1 using stainless steel tweezers.
4. Place the saturated paper onto the sample, and let stand for 30 seconds.

5. Add one drop of the KI solution prepared in step #2 to the paper. A positive test will turn the filter paper yellow, and a negative test will result in either no reaction or a dark brownish-red color paper.
6. Thoroughly rinse the sample with distilled water to remove all traces of nitric acid.

12. TIN

12a. Description

Tin is a soft and ductile white metal similar in appearance to lead, and rarely found in native form. It exists as three *allotropes*: white tin, which is stable at room temperature; gray tin, stable at temperatures below 13.2°C; and brittle tin, found at temperatures above 161°C. On account of its low melting point, 232°C and resistance to corrosion, tin is commonly used for plating or *tinning*. Tinning is especially common on jewelry, because it serves as a protective oxide coating for the underlying metal (Cronyn, 1990).

Although objects of pure tin such as coins are prevalent in the archaeological record, tin itself is much too soft for most purposes and was often mixed with lead to form pewter. The percentages of tin and lead in pewter varied with the availability of each metal during production and the physical properties desired. Adding a higher percentage of tin to the mix made harder pewter. Since lead salts are now known to be cumulative poisons, lead is excluded from modern pewter (Hodges, 1974)

12.b. Deterioration

1. Although tin is a base metal, it is resistant to reoccurring corrosion because of a hard tin (IV) oxide layer which forms on the surface of the metal when in contact with oxygen.
2. Moisture from unstable environments may penetrate the tin (IV) oxide protective layer, and cause continued corrosion in the form of tin oxide and tin (II) oxide. This will result in disfiguring of the object surface or formation of a corrosion crust.
3. Extended periods of cold or heat will cause white tin to change allotropes causing pitting or complete crumbling of the object.
4. Thin coatings of tin over another metal of higher *nobility* are subject to acidic and basic attack due to anodic sacrifice of tin.

12.c. Visual Characterization

Tin, lead, and pewter metals and their corresponding corrosion products are visually difficult to distinguish from each other. Therefore, physical and chemical property tests should be applied to distinguish between them. Archaeological pewter objects exhibit the same forms of corrosion as mentioned below. Common corrosion characteristics of tin are roughness, pitting, swelling, and cracking.

Grey, dull or shiny patina- indicative of a tin (IV) oxide protective corrosion layer that forms in ideal conditions without severe temperature changes or moisture variance.

Black spots, pitting, or warts- Characteristic of an object from a wet environment, and is caused by chlorides or sulfides in the soil which permeate the tin (IV) oxide layer and form Sn(II)S and additional tin (IV) oxide. These black spots appear on the surface of the object in the form of swelling or pitting.

Grey or white crust- Composed of a mixture of tin oxides and possible calcium carbonate deposits, and indicates an advanced state of corrosion. Objects from an alkaline environment are typically encrusted with calcium carbonate, because of the salt deposition potential caused by carbonic acid present.

Roughness (especially on the edges)- tin from a wet environment will exhibit this type of decay, and marks an advanced state of corrosion. Edges of the object may look worn away.

Isolated pits of gray powder or cracking- Due to allotropic conversion of tin, and caused by extreme temperature changes in the buried environment. Small fractures on the surface may also be caused by mineralization. In some cases the object may crumble.

12.d. Chemical Identification

12.c.1. Tin Sulfide Indication (an adaptation of Odegaard et al, 2000)

This test is performed by placing a drop of acid directly onto the sample. Keep in mind that nitric acid will etch the object, therefore an inconspicuous spot should be chosen for testing.

Theory

Sulfuric acid is used to oxidize tin into solution, and sulfur dioxide, formed in situ from the reaction of sulfuric acid and sodium hydrosulfite, reacts in turn with the oxidized tin to form black tin sulfide.

$$H_2SO_{3\,(aq)} \rightleftharpoons SO_{2\,(g)} + H_2O_{(l)}$$

$$Sn^{2+}{}_{(aq)} + SO_{2\,(g)} \longrightarrow SnS_{(s)} + O_{2\,(g)}$$

Equipment

Glassware
Deionized water
Concentrated Sulfuric Acid
Sodium hydrosulfite
Gloves and goggles
Fume hood, or other means of adequate ventilation

Instructions

This reaction should be carried out under a fume hood. Refer to Appendices I and II for additional chemical safety information and waste disposal associated with this procedure.

1. Prepare solution A, a 6M sulfuric acid solution, by slowly adding 10mL concentrated sulfuric acid to 20 ml distilled water while stirring with a glass rod. **Always add acid to water**.
2. Prepare solution B by dissolving 7.8g of sodium hydrosulfite in enough deionized water to make a 100mL solution, and adding 4mL concentrated sulfuric acid to this solution.
3. Now mix 1 part solution A with 4 parts solution B to prepare the final solution. Keep in mind that only a drop of solution is needed to perform each test.
4. Place one drop of test reagent onto the surface of the sample, and let stand for 5-8 minutes. If tin is present, the test reagent will form a black ring of tin sulfide around a beige-colored spot.
5. Thoroughly rinse the sample with distilled water to remove all traces of acid.

13. PLASTICS

There are thousands of different types of synthetic polymers available today, and, in the United States, we use more synthetic polymers, annually, than copper, steel, and aluminum combined (Williamson, 1999). Synthetic polymers, or plastics, are primarily made up of carbon, oxygen, and hydrogen in varying percentages. Many plastics also contain other elements, such as nitrogen, chlorine, and silica, to name a few. Chemists often add dyes, fire retardant, lubricants, or *plasticizers* to the base plastic to attain desired physical and chemical properties. These broad variances in chemical composition and structure cause major differences in degradation mechanisms and resistance. Many factors affect the deterioration of plastic, but water, UV light, and physical stress generally break it down. These degradation agents carry enough energy to break the polymer chain, leading to oxidation of the plastic. In the buried environment, physical stress, organic acids, and moisture catalyze deterioration.

13.a. BAKELITE (Phenol formaldehyde)

Bakelite is the trade name for plastics originally produced by the Bakelite Limited in England and Bakelite Corporation in America, and is frequently used as the generic name for a polymer of phenol and formaldehyde. This *thermosetting* plastic became commercially available to the USA in 1909, and was used until 1920 as a laminate for paper and fabric materials (Blank, 1990). Phenolic molding technology developed in 1920 resulted in widespread use of this plastic. Due to its excellent insulating properties, bakelite was widely used as an electrical or heat insulator.

13.a.1. Visual Characterization

Dark brown/black/maroon color- up until 1923, when clear or light colors could be produced, bakelite was only available in dark colors due to the high heat needed during manufacture of the plastic. Exposure to heat or light will darken the plastic even more.

13.a.2. Hot Needle Test (refer to appendix III for procedure)

Hard to melt- only a slight pinprick will appear on the button as a result from the test.

Fishy or formaldehyde odor- this smell may sometimes be produced by submerging the sample in warm water or rubbing it with your hands. The fishy smell is from carbolic acid vapors.

13.b. CASEIN

Casein is a *thermoplastic* resin formed by combining the casein from milk with formaldehyde and was first commercially produced during 1900 in Germany and 1919 in the United States. Casein is the main protein in milk, and is separated from it by a curdling process that is generally catalyzed through the use of sulfuric acid or rennet. Formaldehyde is then added to the curd to produce plastic. Casein, which exists in a multitude of colors, is often used for manufacturing imitation tortoiseshell, jade, and lapis lazuli.

13.b.1. Visual Characterization

High brilliancy- only seen if the object is in an non-degraded state.

Surface crazing- caused by exposure to excess moisture.

Tool marks- most casein objects are hand or machine carved.

13.b.2. Hot Needle Test (refer to appendix III for procedure)

Burnt milk or hair odor- a smell characteristic of burning proteins.

Browning of plastic- permanent ridge with a tiny brown colored hole after testing.

Slightly difficult to melt- needle will penetrate the surface after slight resistance.

13.c. CELLULOID (Cellulose Nitrate)

Celluloid is an inflammable thermoplastic made from cellulose treated with nitric and sulfuric acids, with camphor commonly used as a *plasticizer*. Celluloid was patented in the United States during 1869, and by the early 1870's it became a popular ivory substitute. Early production of cellulose nitrate was generally limited to plastic in the form of thin sheets (Blank, 1990).

13.c.1. Visual Characterization

Ivory appearance- distinguished from ivory by lack of grain in plastic.

Yellowing- deterioration marker caused by oxidation of the plastic.

Acidic droplets on surface- drops of nitric acid form on the surface, due to an advanced state of degradation. PH indicator paper can be applied to the object surface to check acidity.

13.c.2. Hot Needle Test (refer to appendix III for procedure)

Smoke

Mothball (camphor) odor- rubbing the object with warm hands may also produce this smell.

Easy to melt- needle will penetrate quickly.

13.d. RUBBER

Meso-Americans are known to have produced latex rubber, a thermoplastic, derived from the South American rubber tree, *Hevea brasiliensis*, as early as 1600 BCE. It came into popular use amongst European settlers in the Americas during the mid-eighteenth century, after Charles Goodyear developed a vulcanization process involving sulfonation to transform natural rubber into a more durable thermosetting plastic. Trade restrictions of World War I led Germany to develop the first synthetic rubber composed of a styrene-butadiene copolymer. There are hundreds of different types of natural and synthetic rubbers available today.

13.d.1. Visual Characterization

Fine cracking- indicative of stress cracking caused by loss of plasticity, a common symptom of rubber.

Sticky and viscous body- marks an advanced state of deterioration

Black, gray, or white- common colors of rubber. An off-white or light gray color is characteristic of natural rubber.

13.d.2. Hot Needle Test (refer to appendix III for procedure)

Smoke

Burning rubber or sulfur odor- a sulfur smell is caused by vulcanized rubber.

Easy to melt- the needle will penetrate quickly.

13.e. Linoleum

Linoleum is a floor covering invented by Fredrick Walton in 1863.. Walton established the first commercial linoleum factory in England during 1864. It was an instant success due to its heat and sound insulating qualities, and by 1872 production started in the United States. Linoleum was and still is produced in a variety of colors. However, wood flour and cork additives make linoleum too brown to create deep blue, purple, or pure white colors (Jester 1995).

During manufacture, an organic binder consisting of a 1:4 mass ratio of pine rosin or kauri gum to linseed oil is mixed with ground cork, wood flour, or both, and pigment(White et al, 1994). The mixture is then pressed onto a burlap backing and formed into sheets. The final product is allowed to set for many weeks. During this time, the linseed oil oxidizes to form polymerized linoxyn, and becomes harder and more durable.

13.e.1 Visual Characterization

Flexibility and leather-like appearance- damp environments will saturate and degrade cork and woodflour in linoleum. Swelling, warping, and increased pliability may also result. Alkaline conditions will break down the linoxyn polymers and catalyze deterioration of cork and woodflour, causing increased softness.

2-6 mm thick- typical thickness of commercial linoleum. Although deterioration may cause shrinking or swelling.

Pitting- caused by excessive abrasion from dirt and grit during use or while buried. Alkaline environments may also cause pitting to occur on unevenly mixed linoleum

Fabric backing- linoleum is backed with canvas that is usually coated with red oxide (Jester 1995). In an archaeological context, the body and backing are prone to separate especially in wet environments. This backing may also deteriorate completely.

Brittle structure- the effect of the continued oxidation of linseed oil to form cross-linking. This type of deterioration is common in dry aerobic environments.

Brown or dark appearance- linoleum darkens over time due to the continued oxidation of linseed oil. Staining by tannates or other chemicals in a wet environment will also cause darkening to occur.

Geometric design- characteristic of inlaid linoleum, which was first produced during the late 1890's.

Imitation rock or striated streak design- characteristic of linoleum produced after 1879.

Appendix I: Chemical Safety Information

Ammonium Hydroxide (Household Ammonia): A colorless volatile liquid with a pungent odor that is corrosive and toxic. Ammonia causes severe burns to the skin and eyes, and its vapor is a respiratory irritant. Avoid breathing fumes and contact with skin.

Chromium Trioxide: A dark red crystal at room temperature, which is a probable human carcinogen and severely irritating to the skin and mucous membranes. Along with irritation, Chromium trioxide will cause staining to the skin so gloves are recommended when handling.

Hydrochloric Acid: A colorless or yellowish fuming liquid that is corrosive and toxic. Hydrochloric acid causes severe burns to the skin, eyes, and respiratory system. Wear acid-resistant gloves and goggles, and avoid breathing fumes when handling.

Nitric Acid: A colorless or pale yellow fuming liquid, which is highly corrosive and toxic. This liquid can severely burn the skin and eyes, and its vapor is an extreme respiratory irritant. It should never be mixed with acetone, acetic acid, or alcohol, because violent reactions will occur. Wear acid-resistant gloves and goggles, and avoid breathing fumes when handling (Sease, 1992).

Sodium Hydrosulfite: A white or grayish crystalline powder, which is a slight irritant and flammable. Care should be used while handling this material.

Sulfuric Acid: A clear, colorless, and oily liquid, which is corrosive and toxic. Sulfuric acid causes severe burns to the skin, eyes, and respiratory system. It should never be mixed with acetone, acetic acid, or alcohol, because violent reactions will occur. Wear acid-resistant gloves and goggles, and avoid breathing fumes when handling.

Potassium Iodide: A white crystal that is a mild skin and respiratory irritant. This substance will cause staining of the skin so care should be used while handling it.

Appendix II: Waste Disposal

Calcareous materials identification

1. Unwanted acid can be disposed of by slowly adding small amounts of sodium bicarbonate to the acid until neutralized. The pH of the solution can be monitored with pH indicator paper. Small amounts of non-neutralized acid can be washed down the drain with excess water.

Copper amine indication
1. The 8M nitric acid solution is stable when stored in an acid-resistant container at room temperature.
2. Unwanted acid can be disposed of by slowly adding approximately 0.4 g of sodium bicarbonate per ml of concentrated nitric acid. Check the acidity of the solution with pH indicator paper to ensure neutralization before disposing down the drain. Small amounts of non-neutralized acid can be washed down the drain with excess water.
3. Do not mix ammonia and nitric acid together when disposing.

Silver chromate indication
1. Sulfuric acid is stable when stored in an acid-resistant container at room temperature.
2. Unwanted acid can be disposed of by slowly adding approximately 0.03 g of sodium bicarbonate per ml of 15% acid. Check acidity of the solution with pH indicator paper to ensure neutralization before disposing down the drain. Small amounts of non-neutralized acid can be washed down the drain with excess water.
3. Do not mix ammonia and sulfuric acid together when disposing.
4. The miniscule amount of chromium trioxide used in this experiment may be safely disposed of down the drain with excess water.

Iron (III) chloride indication
1. Hydrochloric acid is stable when stored in an acid-resistant container at room temperature.
2. Unwanted acid can be disposed of by slowly adding approximately 0.6g of sodium bicarbonate per ml of concentrated acid. Check acidity of the solution with pH indicator paper to ensure neutralization before disposing down the drain. Small amounts of non-neutralized acid can be washed down the drain with excess water.

Lead-iodide indication
1. The 0.5M nitric acid solution is stable when stored in an acid-resistant container at room temperature.
2. Unwanted acid can be disposed of by slowly adding approximately a 0.03g of sodium bicarbonate per ml of 0.5M nitric acid. Check acidity of the solution with pH indicator paper to ensure neutralization before disposing down the drain. Small amounts of non-neutralized acid can be washed down the drain with excess water.
3. Small amounts of potassium iodide may safely disposed of down the drain with excess water.

Tin sulfide indication
1. 6M sulfuric acid, solution A, is stable when stored in an acid-resistant container at room temperature.
2. Any unused portions of solution B and the final test reagent solution should be disposed of by slowly adding approximately 2g of sodium bicarbonate per ml of acid used. Check acidity of the solution with pH indicator paper to ensure neutralization before disposing down the drain. Small amounts of non-neutralized acid can be washed down the drain with excess water.

Appendix III: Hot Needle Test (adapted from Identifying and Testing for Materials, 2000)

The hot needle test is a destructive test developed for the use of plastic characterization. Thus, it should be performed on an inconspicuous area of the test sample. It is a good idea to have reference samples of known composition on hand to use for comparison. Practicing with a hot needle on reference samples will give you a better feel concerning what to look for when conducting the test on samples of unknown materials.

Equipment
Needle
Heat source (candle or blow torch)
Reference samples

Instructions
1. Heat the needle until the point is red hot. The needle should be held with a pliers or cork to prevent burning your fingers.
2. Touch the needle to the sample surface for a second. Observe the smell, amount of smoke produced, and needle penetration.

Appendix IV: Machery-Nagel Products Suppliers

Macherey-Nagel Inc.
6 South Third St.
Suite 402
Easton PA 18042
Phone: 001 610 559 9848
e-mail: sales-us@mn-net.com

Gallard-Schlesinger Industries, Inc.
777 Zeckendorf Blvd.
Garden City, NY 11530
Phone: 001 516 229 4000
e-mail: info@gallard.com
<www.gallard.com>

Appendix V: Decision Tree

This decision tree outlines the characterization process recommended by the author. Visual and physical characterization steps are represented by solid one-headed arrows, while chemical and physical test steps are represented by dashed two-headed arrows. Text in parentheses refer to sections with relevant characterization or identification information. If a material can not be identified (other) using this tree, one should consult with a specialist or conservator.

Glossary

Acidic Oxide a covalent oxide that dissolves in water to produce an acidic solution, ph <7.0.

Allotropy the ability of an element to exist naturally in different states, such as crystalline structures.

Alloy a metallic material composed of two or more metals that are generally combined in the molten state.

Anodic sacrifice the occurrence of a metal serving as the reducing agent in a galvanic reaction. This often leads to the dissolution of a solid metal.

Basic Oxide an ionic oxide that dissolves in water to produce a basic solution, ph >7.0.

Caliche a cement-like substance of precipitated calcium carbonate and calcium sulfate.

Cathodic protection the event, in a galvanic reaction, of a metal being protected from oxidation by receiving electrons from a sacrificial anode.

Clay hydrous aluminum silicate generally commingled with powdered feldspar, quartz sand, iron oxides, and various other minerals.

Corrosion a series of chemical or electrochemical reactions with metal that lead to the loss of metallic properties and the formation of mineral incrustations.

Dentine a mineralized dental tissue composed of 1:3 collagen: hydroxyapatite with 10% water by weight (Cronyn, 1990).

Electrolyte an ionic water soluble material that dissolves to give an electrically conductive solution.

Gilding the application of a thin layer of gold to the surface of an object.

Grog previously fired ceramic fragments used as temper in ceramic production.

Metal Core the inner unaffected portion of a corroded metal object, which is encompassed by the outer corroded layer.

Molarity (M) the concentration of a solution expressed as moles of solute per liter of solution.

Native Metal a metal that occurs in nature in its elemental form uncombined with any other elements, such as gold, silver, or copper. Other metals, like iron, lead, or tin occur only as compound ores.

Noble Metal a metal with a standard electrode potential that is greater than that of hydrogen. Metals are ranked on a nobility scale determined by their standard electrode potentials. The following is a partial list of metal nobility, in increasing order, with gold being the noblest:

Mild steel, wrought iron
Cast iron
Lead-tin alloys
Lead
Tin
Brass
Copper
Bronze
Silver
Gold

Oxidation loss of electrons from a species during a chemical reaction

Patina there are two types of patina: artificial patination, which is applied for aesthetic reasons or protection of the underlying metal, and natural patina, which is a uniform thin layer of corrosion product produced by a natural environment.

PH the negative logarithm of the hydrogen ion concentration in a solution. In other words, it is the measure of acidity or alkalinity of a solution on a scale of 0-14. Seven is neutral on this scale, with 14 being basic, and 0 being acidic.

Phloem complex plant tissue of the vascular system involved in the conducting of sap.

Pickling the use of a diluted acid to either remove a certain component of an alloy from the surface of an object, or to clean an object after casting.

Plasticizer a substance incorporated into another material (usually a plastic) to increase its flexibility, workability, or distensibility.

Plating a thin layer of metal that has been deposited on the surface of another metal by various physical or chemical processes.

Sizing a solution of gelatinous material, usually glue, casein, wax, or clay used as an adhesive employed when sheathing an object with another material.

Sulfur Reducing Bacteria anaerobic bacteria that reduce sulfates to sulfides.

Tarnish thin film of oxidation that causes staining on the exposed surface of a metal.

Tawing a process of leather making that employs alum and salt to replace water in skin.

Thermoplastic a plastic composed of linear macromolecules that are amorphous and soften at high temperatures.

Thermoset Plastic a plastic, which under heat and pressure, polymerizes into a form that cannot be re-softened due to crosslinking of the molecules. Therefore, it can withstand generous amounts of heat, and is used for making such things as ashtrays, pot handles, and electrical parts.

Tinning an application of molten tin or tin alloy to another metal, to produce a thin coating. Tinning is often an alloy, because it produces a lower melting point, which is easier to work with.

White Metal an alloy of tin, zinc, or lead, and is white in appearance. Generally refers to an alloy primarily composed of tin.

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Senior Research Paper
Fall Semester 2001
Anthropology 3028
Department of Anthropology
University of Minnesota